Shock response of Cu/graphene nanolayered composites

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A B S T R A C T
Shock response of Cu/graphene nanolayered composites is investigated with molecular dynamics simulations, including deformation and spall damage of Cu, and delamination of the nanolaminates, as well as wrinkling, fracture and perforation of graphene, for parallel and normal shock loading. The Cu (111)/graphene interface is the source of dislocations in Cu and barrier to their propagation, and nucleation sites follow the Moiré/C19 pattern. Direct transmission of dislocation across graphene is not observed. Spallation occurs at the Cu/graphene interface with a reduced tensile strength. Under strong shock loading, graphene forms wrinkles and folds upon compression, and fractures upon release and tension for parallel shocks, while it is perforated by Cu atoms for normal shock loading via defect formation in graphene at high temperatures.

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1. Introduction

Graphene [1], with high Young's modulus (1 TPa), high intrinsic strength (130 GPa) and light weight [2], has great potential as a reinforcing component in composites, and has been widely used in polymer hosts [3–5]. Effective enhancement in strength and toughness was reported for various polymers including polyurethane [6], allylamine [7], and cellulose [8], which depends on such factors as structural imperfections and stress transfer at the interfaces [9,10]. Compared to polymer/graphene composites, metal/graphene composites have not been investigated adequately, since it is technically more difficult to fabricate such composites given the negligible solubility of graphene in metals. Nevertheless, some metal/graphene composites with significantly improved tensile and yield strength [11,12], e.g., Al and Cu/graphene composites, were successfully fabricated recently [11–13]. Cu/graphene composites with uniform dispersion were obtained via applying rolling process to graphene-covered Cu powders, or accumulative roll bonding to graphene-covered microstrips [14,15]. These Cu composites exhibit tensile strengths of 496 MPa [15], and hardness up to 39% higher than pure copper [14]. Recently, a nanolayered Cu/graphene composite was synthesized [16], and a nanopillar of this composite shows exceptional strength under nonshock loading conditions as shown by experiments and molecular dynamics (MD) simulations, since dislocation propagation across the interface was effectively blocked by graphene [16]. Another MD simulation work revealed its outstanding resistance to radiation damage [17]. Cu/graphene nanolayered composites are also promising for impulsive loading such as high-speed impact. MD simulations showed that incorporating graphene leads to improved penetration resistance [18,19]. In graphene-reinforced composites, structure and properties of the interfaces are the key factors that determine their overall performance [10,16,17,19]. Rich shock phenomena of deformation and damage remain to be revealed, and a complete understanding of the underlying mechanisms, including the role of Cu/graphene interface (CGI), is still lacking. For instance, while CGI can be an effective barrier to dislocations, its possible role as a dislocation source is neglected. Additionally, CGIs are common in graphene-based electronic devices [20], and their impact response is directly relevant to their performance under harsh environments. Thus, shock-induced damage of Cu/graphene nanolaminates is also of practical interest.

In the present paper, we conduct MD simulations to investigate...
shock response of Cu/graphene nanolayered composites (or simply nanolaminates), including deformation in Cu, spall damage of the nanolaminates, and wrinkling, fracture and perforation of graphene. Shock loading is applied perpendicular or parallel to CGI to investigate the anisotropy of shock response.

2. Methodology

Cu/graphene nanolayered composites as in Fig. 1(a) consist of single crystal Cu and graphene. The coordinate system is defined in terms of Cu crystallographic orientations as x: [110], y: [112], and z: [111]. The graphene layer is sandwiched between two Cu (111) planes, with its zigzag and armchair directions aligned with the x- and y-axes, respectively. Lattice mismatch between one unit cell on Cu (111) plane and that in graphene is about 4.5%. To minimize the mismatch, we construct a configuration of 23 × 23 graphene unit cells on 22 × 22 Cu (111) unit cells. The resultant mismatch between Cu (111) and graphene is about 0.07%. Lateral elongation of C–C bonds is minimized. Incommensurate overlay of graphene on Cu (111) induces a hexagonal Moiré pattern at CGI (Fig. 1(b)). The hexagonal superstructure has a periodicity of 5.5 nm, which agrees well with the experimental value of about 6 nm measured with scanning tunnel microscopy [21,22]. Three typical sites exist in the Moiré superstructure, i.e., hollow (H), top (T), and intermediate (I) (Fig. 1(b)), representing different positions on the graphene layer occupied by Cu atoms (Fig. 1(c)) [23]. As a result, their potential energies are different, and the potential energy map shows a similar Moiré pattern (Fig. 1(d)).

We use the Large-scale Atomic/Molecular Massively Parallel Simulator [24] for MD simulations. Cu/graphene nanolayered composites with x × y × z dimensions of approximately 100 × 10 × 20 nm³, 10 × 100 × 20 nm³, and 10 × 10 × 120 nm³ are constructed, for shock loading along the x-, y-, and z-directions, respectively. The interaction between C atoms is described by the adaptive intermolecular reactive empirical bond order (AIREBO) potential [25], and that between Cu atoms, by the embedded atom model potential [26]. A Lennard-Jones potential with parameters of 25.78 meV and 3.0825 Å is used to describe the van der Waals interaction between C and Cu [17,27].

Before shock loading, all the composites are thermalized at 300 K and zero pressure with the constant pressure-temperature ensemble, and a time step is 1 fs for integrating the equation of motion. The free surface condition is applied to the ends of the composites along the shock direction, and periodic boundary conditions, along the lateral directions. We use the microcanonical ensemble for shock simulations [28,29]. Symmetric impact is adopted to simulate spallation, and details were presented elsewhere [30]. For other shock simulations, an initial particle velocity, −v₀, is assigned to a composite, and its impact on a rigid wall induces shock wave propagation into the composite. The time step for integrating the equation of motion is 0.1 fs for high velocity impact (e.g., v₀ > 2.0 km/s), and increases up to 1 fs with decreasing v₀. Shock loading is applied either normal or parallel to the graphene layer to investigate the effects of CGI orientation, referred to as normal and parallel shock loading, respectively. For real life impact applications, the impact velocity ranges from 100 m/s to 10 km/s [31], and our simulations are conducted within this range.

The atomic–lattice deformation can be characterized with the slip vector in terms of the maximum relative displacement [32,33].

$$\mathbf{s}_i = \mathbf{x}_{ij} - \mathbf{X}_{ij} = |\mathbf{x}_{ij} - \mathbf{X}_{ij}|_{\text{max}}$$

Here \(\mathbf{x}_{ij}\) and \(\mathbf{X}_{ij}\) are the vector difference in the positions of atom i and its nearest atom j in current and reference configurations, respectively. The reference configurations are the initial structures at zero strain. The total slip scalar follows as \(s_i = |\mathbf{s}_i|\). The local structure around an atom is also characterized with the Ackland method, based on which atoms are classified into face centered cubic (fcc), hexagonal close-packed (hcp), or unknown types [34].

MD simulations yield trajectories from which some physical properties can be extracted. Given our shock simulation geometry, we divide the simulation cell into fine bins only along the shock direction, and the average physical properties are obtained within each bin (the 1D-binning analysis [30]), such as stress tensor \(\sigma_{ij}\) and particle velocity profiles. The center-of-mass velocity of a bin is removed when calculating stress. Stress for each bin is the averaged virial stress plus thermal contributions.

3. Results and discussion

3.1. Deformation at CGI upon shock compression

3.1.1. Normal shocks

Upon compression by normal shocks, dislocations nucleate heterogeneously at CGI in Cu, since the potential energies of Cu atoms are different, decreasing in the order of T, I, and H (Fig. 1(d)). For \(v_0 < 0.8 \text{ km/s}\), both Cu layers around CGI and graphene deform elastically. When \(v_0 = 0.8 \text{ km/s}\), Cu dislocations nucleate at T sites on Cu (111) layer immediately adjacent to graphene. At higher \(v_0\) (1.0 km/s), dislocations nucleate on T sites first and then on I sites. For such weak shocks, dislocations only form at CGI. For \(1.0 < v_0 < 1.7 \text{ km/s}\) above the Hugoniot elastic limit of single crystal Cu shocked along [111], a plastic wave forms and propagates behind the elastic precursor. Dislocations are induced by the elastic precursor at CGI before the arrival of the plastic wave.

At \(v_0 \geq 1.7 \text{ km/s}\), the faster-propagating plastic shock wave originated at the impact plane arrives at CGI before dislocations nucleate at CGI, because the incubation time is shorter than those for weaker shocks, and is insufficient for dislocation nucleation by the elastic wave (Fig. 2(a) and (b), 9.5 ps). Dislocations due to the plastic shock wave arrive at CGI but are blocked by CGI (Fig. 2(b), at 9.5 ps). At 9.7 ps, a Shockley partial dislocation, \([\text{T21}]/[\text{111}]\),...
nucleates on the right side of graphene (Fig. 2(b); indicated by the black arrow). At 10.5 ps, dislocation density on the right side increases to a level to form a plastic wave.

In order to reveal the role of CGI in the dislocation activities, we plot the total slip maps of the first Cu layers to the left (Fig. 2(c)) and right (Fig. 2(d)) of graphene; the hexagonal pattern is absent in the former but marked in the latter. The nucleation of dislocations on the right side occurs in a region consisting of T and I sites with high potential energy (Fig. 2(d), 9.7 ps), and is independent of the dislocations on the left side. More dislocations nucleate on the right side from the T or I sites (Fig. 2(d), 10.5 ps) as stress concentration builds up at CGI.

3.1.2. Parallel shocks

For parallel shocks, shock wave propagates along the graphene sheet confined between two Cu (111) planes [35]. The in-plane Young’s modulus of graphene is much higher than that of Cu. Therefore, the strain in graphene after shock is smaller than that in Cu, and the lattice mismatch is reduced in the shock direction, giving rise to the Moiré pattern changes. Fig. 3(a) and (b) present the Moiré patterns formed by graphene and the lower Cu plane before and after shock at \( u_p = 0.6 \) km/s, respectively. Before shock arrival, the hollow site configurations (H) in the Moiré pattern are hexagonal, and the hexagons collectively show a three-fold symmetry (Fig. 3(a)). They become two parallel rectangles along the shock direction after shock passage (Fig. 3(b)). For parallel loading, the potential energy distribution on Cu surface layer shows different characteristic from normal loading: it is higher on hollow sites than on top or intermediate sites (Fig. 3(c)), likely due to differences in packing between graphene and Cu.

For parallel shock loading at \( u_p \geq 0.6 \) km/s, CGI is also the preferential site for dislocation nucleation in Cu. Slip system [112]/(111) is activated first. Dislocations form initially on one side of graphene (primary dislocations), and induce secondary dislocations on the other side via wrinkling of graphene (Fig. 4(a) and (b)). As shown in Fig. 4(b), a primary dislocation propagates downward from CGI, while the secondary dislocation on the same slip plane propagates in the opposite direction. Thus, the secondary dislocation is not simply the transmission of the primary one. While the primary dislocations all nucleate on high potential energy sites (Fig. 4(c)), the dislocations on the other side either nucleate on such sites or are induced by the primary ones via strain concentration at CGI (Fig. 4(d)).

CGI serves as a barrier or nucleation site for dislocations in the Cu/graphene nanolaminates, consistent with a previous work on nanopillars under nonshock loading [16]. Dislocations emit from nucleation sites on the right side of graphene (Fig. 2(b); indicated by the black arrow). At 10.5 ps, dislocation density on the right side increases to a level to form a plastic wave.

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CGI under shock loading, e.g., at T or I sites of corresponding Moiré patterns for normal shocks, and at H sites for parallel shocks. A blocked dislocation, or a dislocation initiated from CGI, may induce a secondary dislocation on the other side via stress concentration. However, direct transmission of dislocation across CGI is not observed.

3.2. Delamination at CGI

We adopt symmetric impact [30] to investigate spallation of the Cu/graphene nanolaminates. Under normal shock loading along the z-axis, graphene is placed in the target mid-section on the xy-plane. Stress evolution demonstrated in a traditional x–t diagram (Fig. 5) shows shock compression, release, tension, and spallation; the rarefaction or release fans from free surfaces of the flyer and target encounter at CGI. Incipient spall occurs at \( u_p = 0.2 \) km/s, and the incipient spall strength (maximum tensile stress right before spall) is obtained as 7.9 GPa by 1D binning analysis. The spallation is actually delamination at CGI (Fig. 5 inset). Graphene is wrinkled under tension, and recovers its shape after complete separation at ~21.5 ps, while Cu remains elastic during the whole process.

Under parallel shock loading (e.g., along the x-axis), incipient spall occurs at \( u_p = 0.4 \) km/s, along with CGI delamination (Fig. 6). The release fans from the free surfaces of flyer and target encounter at ~17 ps, inducing the maximum tensile stress. At 20 ps, dislocations nucleate at CGI and grow. Since there is a tensile stress component perpendicular to CGI, delamination is resulted (24 ps). For higher impact velocities, e.g., \( u_p = 0.8 \) km/s, delamination is accompanied by void nucleation in Cu. The incipient spall strength obtained via 1D binning analysis is 10.8 GPa, higher than the normal shock case (\( u_p = 0.2 \) km/s, 7.9 GPa).

For normal shocks, interfacial delamination is simply debonding, and can occur without plastic deformation in Cu, while in the parallel shock case, spall involves both transverse delamination and tensile damage of Cu, leading to higher spall strength. However, CGI lowers the barrier to dislocation nucleation in Cu, so the incipient spall strength is reduced compared to single crystal Cu under shock loading along the same direction ([110], at \( u_p = 0.5 \) km/s, 15 GPa) [30]. Therefore, graphene weakens the spall strength of Cu, regardless of the loading direction.

3.3. Graphene deformation and damage by strong shocks

Graphene undergoes deformation or damage in the forms of wrinkling, fracture and perforation induced by shock loading. Wrinkling and fracture are observed for parallel shocks, while perforation occurs for normal shocks.

3.3.1. Wrinkling and fracture

Suspended graphene, with low bending stiffness, can readily wrinkle or fold under in-plane compression or other perturbations [36]. In the Cu/graphene nanolaminates, its out-of-plane movement is confined by Cu, so graphene remains flat for parallel shocks at \( u_p < 0.4 \) km/s. Wrinkling occurs in conjunction with delamination at \( u_p > 0.4 \) km/s, and due to dislocations in neighboring Cu layers for \( u_p > 0.6 \) km/s. At even higher impact velocities (\( u_p > 1.0 \) km/s), graphene wrinkles voluntarily despite Cu confinement. Here we take a parallel shock run with \( u_p = 2.0 \) km/s as an example.

Figure 7 shows the generation and evolution of wrinkles and folds. Three segments of graphene, as noted with A–C, can be identified. Point C delimits wrinkled regions in the elastically compressed region (BC) and unshocked flat region. Point B separates the elastic (BC) and plastic (AB) shock regions, where ripples/wrinkles and folds form, respectively (Fig. 7(a)). Ripples (I) and folds (II and III) are defined graphically in Fig. 7(c). In the BC segment, the formation of ripples also gives rise to dislocations above and below the graphene layer. Ripples are compressed to form folds (Fig. 7(b)) in segment AB, i.e., folds 1, 2 and 3. Similar to a previous work [37], C atoms on adjacent layers of fold may rebind under compression, e.g., the black atoms in folds II and III (Fig. 7(c)). The width/length ratio, \( \alpha \), in the compressed region of a graphene ribbon determines whether the growth of wrinkles is chirality-dependent (\( \alpha < 3.0 \)) or isotropic (\( \alpha > 3.0 \)) [38,39]. Periodic
boundary condition imposed in the lateral direction of graphene yields infinite width and thus \( \alpha \), so the growth of wrinkles is isotropic for shocks along the armchair and zigzag directions. Thus, we obtain similar wrinkles for parallel shock loading along the \( x \)- and \( y \)-axes.

A fold forms by pileup of ripples under compression. Sufficiently high pressure and plastic shock velocity are required to drive this folding process. Thus, a fold forms at a higher piston velocity \( (u_p \geq 1.7 \text{ km/s}) \) than that for a ripple \( (u_p \geq 1.0 \text{ km/s}) \). Folding and rebonding of C atoms in graphene may lead to changes in electronic and mechanical properties of graphene-based devices and composites [40,41]. They also play a role in graphene fracture as discussed below.

For parallel shock loading, fracture of graphene occurs during release, as a result of the formation of graphene folds, the friction between graphene and Cu, and tension. The results for parallel shock loading along the \( x \)- and \( y \)-axes are similar, and only the \( x \)-direction loading is discussed below.

Fig. 7(a) shows representative wrinkles of graphene. I is a primitive wrinkle (ripple), and II and III are final forms of wrinkles (folds). Some C atoms from two adjacent C layers are bonded (black C atoms). (A colour version of this figure can be viewed online.)

![Fig. 7. Wrinkles and folds of graphene under parallel shock loading along the \( x \)-axis at \( u_p = 2.0 \text{ km/s} \). (a) \( t = 2.5 \text{ ps} \). (b) \( t = 5.0 \text{ ps} \). Cu atoms are color-coded with slip. (c) Representative wrinkles of graphene. I is a primitive wrinkle (ripple), and II and III are final forms of wrinkles (folds). Some C atoms from two adjacent C layers are bonded (black C atoms). (A colour version of this figure can be viewed online.)](image1)

![Fig. 8. (a) Particle velocity profiles for Cu atoms \( (u_{Cu}) \) and C atoms \( (u_G) \) during release stage and (b) fracture process of graphene at fold 2, from the same run as in Fig. 7. The insets are side views of CGI at corresponding instants. Numbers 1–3, and 2’ denote folds. (A colour version of this figure can be viewed online.)](image2)

release fan interacts with the tail of the incoming release fan and induces tension, and delamination is resulted at the folds.

3.3.2. Perforation

Strong shocks with high impact velocities \( (u_p \geq 3.0 \text{ km/s}) \) induce high temperature, high pressure, and melting of Cu crystal [42]. Graphene perforation by Cu atoms is observed for shocks along the \( z \)-axis at \( u_p \geq 3.5 \text{ km/s} \), corresponding to a shock state in Cu of approximately 7000 K and 275 GPa. Fig. 9 shows the perforation process in detail, beginning at 22 ps. At such a high temperature, thermal fluctuations are pronounced and lead to the formation of a Stone-Wales defect [35] in graphene at 22.2 ps. At 24.0 ps, another Stone-Wales defect forms, and then one of its heptagon combines with a heptagon of the first Stone-Wales defect to form an octagon. At 24.5 ps, the third Stone-Wales defect forms and results in a larger polygon (hendecagon), which supplies sufficient space to allow the penetration of a Cu atom, and is distended as a result (at 24.6 ps). More Cu atoms are forced through and expand the hole (25 ps and 27 ps). A previous work [43] demonstrated that clustering of Stone-Wales defects and subsequent formation of an octagon are the first step to damage and melting of graphene under high temperature, consistent with our MD simulation results. However, wrinkling...
pressure give rise to defect formation in graphene and then upon compression, and fractures upon release and tension for via Cu at the Cu/graphene interface with a reduced tensile strength, either induce a secondary dislocation on the other side. Spallation occurs observed, and a primary dislocation on one side of graphene may pattern. Direct transmission of dislocation across graphene is not barrier to their propagation, and nucleation sites follow the Moir pattern. (similar to Fig. 7) rather than perforation occurs for parallel shocks along the x- or y-axis, even at \(u_{tp} = 4.0 \text{ km/s} (~10000 \text{ K} \text{ and } 340 \text{ GPa in Cu})\), likely because of its lack of in-plane constraint.

4. Conclusions

Under parallel or normal shock loading, rich phenomena are observed in Cu/graphene nanolayered composites, including deformation and spall damage of Cu, delamination of the nanolaminates, and wrinkling, fracture and perforation of graphene. The Cu (111)/graphene interface is the source of dislocations in Cu and barrier to their propagation, and nucleation sites follow the Moir pattern. Direct transmission of dislocation across graphene is not observed, and a primary dislocation on one side of graphene may induce a secondary dislocation on the other side. Spallation occurs at the Cu/graphene interface with a reduced tensile strength, either via Cu–C debonding (delamination) or ductile void nucleation in Cu. Under strong shock loading, graphene forms wrinkles and folds upon compression, and fractures upon release and tension for parallel shocks; for normal shocks, high temperature and high pressure give rise to defect formation in graphene and then perforation by Cu atoms.

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References


